

Chiroptical Studies of Bicyclic α -Diketones¹

Tadeusz Połowski and Zbigniew Dauter

Institute of Organic Chemistry, Technical University of Gdansk, 80-952 Gdansk, Poland

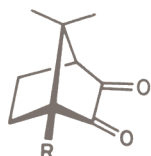
On the basis of crystallographic analysis it was established that the α -diketone chromophore in bicyclo[2.2.1]heptane-2,3-diones is planar. C.d. studies of some bicyclic compounds show that the c.d. sign for long-wavelength transition is governed by the octant rule with signs opposite to that known for ketones. The vicinal effect of substituents with the same location in space strongly influences the magnitude of the Cotton effect, but not its sign.

The chiroptical properties of α -diketones have been the subject of a number of theoretical and experimental studies over the last few years.²⁻¹³ A great deal of effort has been directed toward establishing the relation between Cotton effect (C.E.) sign and molecular geometry. Most of the spectroscopic investigations have been devoted to the two lowest-energy electronic transitions which for *cisoid* α -diketones appear as weak absorptions near 480 and 300 nm. The electronic structure of the α -dicarbonyl chromophore and thus the nature of these transitions seems to be well established now.^{8,14,15} The ordering of the highest occupied molecular orbitals is $n_+ > \pi_+ > n_- > \pi_-$, where subscripts designate symmetric (+) and antisymmetric (-) combinations of interacting carbonyl sub-unit orbitals. The lowest-energy transition can be assigned as nearly pure $n_+ \rightarrow \pi_-^*$ excitation and the second one can be described as an admixture of $n_- \rightarrow \pi_-^*$ and $n_+ \rightarrow \pi_+^*$ states.⁸ All of them are localized on the α -dicarbonyl moiety. The energy separation between the highest filled molecular orbitals n_+ is known to be of the order of 2 eV.¹⁴ The first theoretical study of the optical rotatory properties of skewed glyoxal models suggested that the positive sign of the long-wavelength C.E. corresponds to right-handed helicity (*P*-chirality) of *cisoid* α -diketones.⁴ This interpretation was challenged by Burgstahler and co-workers^{5,7} on the grounds of conformational analysis and crystallographic evidence. They suggested that the dione's inherent chirality cannot be assigned with certainty on the basis of its C.E. sign and that substituents may influence the optical rotatory strength by vicinal effects. The recent theoretical treatment of cyclopentane-1,2-diones attributed the negative C.E. of the

long-wavelength transition to *P* helicity of the twisted dicarbonyl group, and showed a significant role for the vicinal effects of substituents in determining the sign and magnitudes of the C.E.⁸

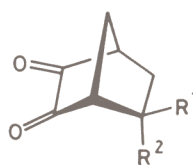
The most frequently studied model is (1*R*)-1,7,7-trimethylbicyclo[2.2.1]heptane-2,3-dione (camphorquinone) (**1a**)^{2,3,10-13} and *M*- (left-handed helicity),³ *P*-,⁴ or *M*- in solution and *P*-chirality in the solid state¹¹ was suggested for its α -dicarbonyl moiety. Recently, Dezentje and Dekkers¹³ calculated rotatory strengths of diones (**1a**), (**1c**), and (**1h**) using a polarizability model. Their results agree well with experiment if planarity of the dicarbonyl group is assumed. *X*-Ray crystallographic studies of compound (**1a**) present some difficulties since crystals of this dione have two molecules in the asymmetric unit;¹⁶ however, Bright *et al.*¹⁷ have recently shown that one molecule in the crystal cell of dione (**1a**) has a planar dione moiety and the second is slightly skewed in the *P*-sense. They also have concluded that the distortion is caused by intermolecular forces in the crystal and that any real deviations from planarity in the free molecule are small.

In this work we performed *X*-ray studies of diones (**1d**) and (**1h**) and we tried to establish whether or not the inherent chirality of the chromophore contributes to the optical activity of bicyclo[2.2.1]heptane-2,3-diones. Next, we synthesized, and studied chiroptical properties of, some new model compounds, especially bicyclo[2.2.1]heptane-2,3-diones (**2**)–(**6**) with disymmetrically placed substituents far from the chromophore. We believe that such a location protects both substituent and chromophore against steric interaction. Finally, we studied c.d. spectra of (**1d**)–(**p**) in order to establish the effect of various substituents on the c.d.



(1)

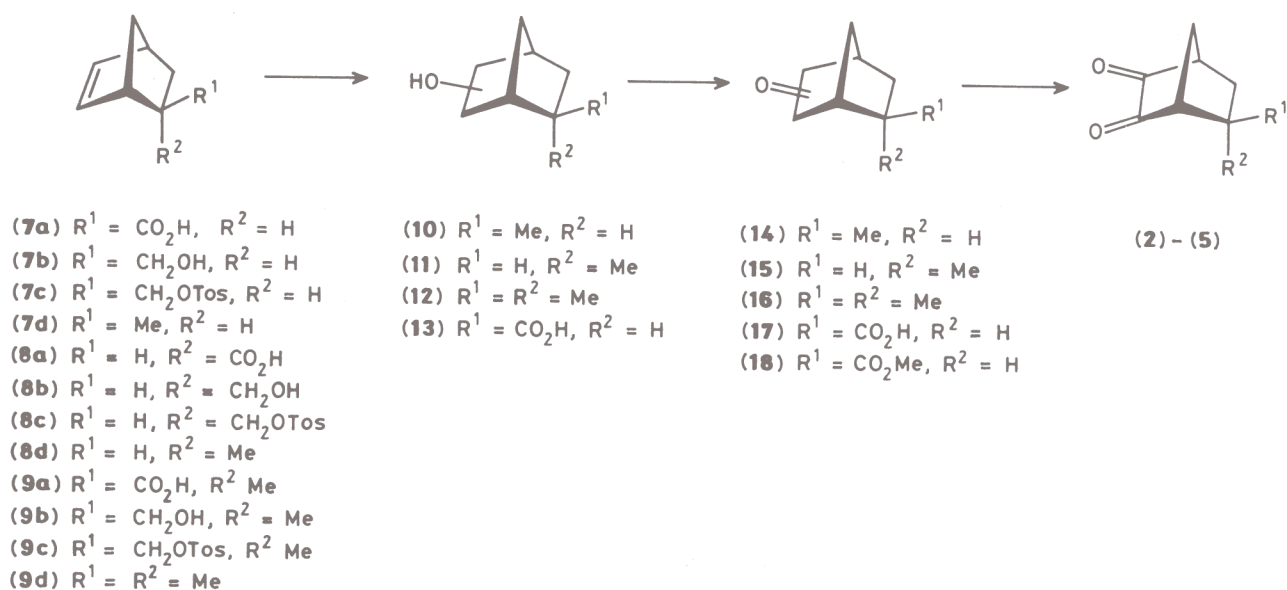
- | | |
|----------------------------|--|
| a; R = Me | i; R = CO ₂ H |
| b; R = H | j; R = CO ₂ Me |
| c; R = D | k; R = NCO |
| d; R = CH ₂ OH | l; R = NHCO ₂ Bu ^t |
| e; R = CH ₂ OAc | m; R = ⁺ NH ₃ |
| f; R = F | n; R = NHAc |
| g; R = Cl | o; R = Ph |
| h; R = Br | p; R = CONH ₂ |



- (2) R¹ = Me, R² = H
 (3) R¹ = H, R² = Me
 (4) R¹ = R² = Me
 (5) R¹ = CO₂Me, R² = H



(6)



Scheme.

Synthesis.—The syntheses of diones (2)–(5) were based on the acids (7a), (8a), and (9a) as substrates, which were resolved by the use of (–)-1-phenylethylamine to obtain (–)-(7a), $[\alpha]_D^{20} -12.1^\circ$ (71% optical purity),¹⁸ (–)-(8a), $[\alpha]_D^{20} -119^\circ$ (81% optical purity),¹⁹ and (+)-(9a), $[\alpha]_D^{20} +58.5^\circ$ (87% optical purity).¹⁸ The absolute configurations of acids (–)-(7a), (–)-(8a), and (+)-(9a) were already known¹⁸ to be as indicated in the Scheme. These acids were converted into cycloalkenes (7d), (8d), and (9d) according to a procedure similar to that reported by Berson *et al.*,¹⁸ via the following reaction sequence: reduction of acids by lithium aluminium hydride to give unsaturated alcohols (7b), (8b), and (9b); acylation with toluene-*p*-sulphonyl chloride to give sulphonates (7c), (8c), and (9c); followed by reduction with LiAlH_4 . Mixtures of *exo*-5(6)-hydroxybicycloalkanes (10)–(12), obtained by addition of mercury(II) acetate to alkenes (7d), (8d), and (9d) and subsequent reduction with sodium borohydride,²⁰ were treated with Jones' reagent to afford mixtures of 5(6)-oxo compounds (14)–(16). Ketones (14)–(16) were oxidized with selenium dioxide to afford α -diketones (2)–(4) as single products. A similar sequence of steps was applied to acid (7a) for the synthesis of (5).

Compound (1e) was obtained by SeO_2 oxidation of 10-acetoxycamphor (19)²¹ and was then hydrolysed to the alcohol (1d).



- (19) $R = \text{CH}_2\text{OAc}$
 (20) $R = \text{CO}_2\text{H}$
 (21) $R = {}^+\text{NH}_3\text{Cl}^-$
 (22) $R = \text{F}$
 (23) $R = \text{Cl}$
 (24) $R = \text{Br}$
 (25) $R = \text{NHAc}$
 (26) $R = \text{Ph}$

The substrate for the synthesis of diketones (1f–h) was (+)-ketopinac acid (20), which is derived from (+)-camphor.^{9,22} After reaction of SeO_2 with (20) the resulting acid (1i)²³ was converted into the corresponding acid azide whose Curtius rearrangement afforded isocyanate (1k) which reacted with *t*-butyl alcohol to provide carbamate (1l). Cleavage of the *N*-*t*-butoxycarbonyl group with trifluoroacetic acid (TFA) gave amine trifluoroacetate (1m). The simpler procedure, also based on the Curtius rearrangement, was used to convert acid (20) into amine (21).²⁴ Amine (21) was converted into halogeno-ketones (22) and (23) through diazonium salts, and the halogeno compounds were oxidized to (1f) and (1g). Phenyl ketone (26), resulting from oxidative decarboxylation of acid (20) with lead tetra-acetate in benzene solution, gave dione (1o) upon treatment with SeO_2 .

Crystal Structure of α -Diketones (1d) and (1h).—The crystal structure of hydroxy dione (1d) is nearly isomorphic with that of camphorquinone (1a)¹⁷ which was described in terms of the non-standard space group *I*2. Figure 1 shows one of the two symmetry-non-equivalent molecules of compound (1d) and the atom-numbering scheme; the second molecule of (1d) has atom numbers increased by 10; the same numbering is adopted in compound (1h). α -Dione moieties in both molecules of (1d) and in (1h) are planar within experimental accuracy. The hydroxy group in both molecules of (1d) is disordered and occupies two positions, nearly identical in both molecules, with torsion angles $+68^\circ$ and -49° . The molecules are packed in the unit cell of compound (1d) in such a way (Figure 2) that hydroxymethyl groups point towards the 2-fold axis and the local symmetry around that axis is approximately 4_2 . Hydroxy groups form intermolecular hydrogen bonds with analogous groups of neighbouring molecules in each of the alternative disordered conformations.

Chiroptical Properties.—C.d. spectra of α -diketones (1)–(6) measured in the long-wavelength region are collected in Table 1. Two C.E.s, corresponding to two $n \rightarrow \pi^*$ transitions, are observed at ca. 480 and 290 nm. Camphorquinone (1a) and related 1-substituted apocamphorquinones (1d–p) exhibit the same c.d. signs in both regions though the magnitude of the C.E.

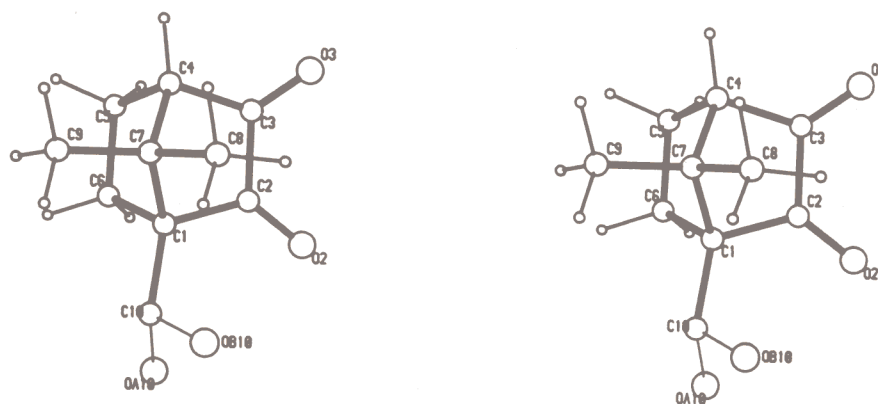


Figure 1. Stereoview of molecule 1 of α -diketone (**1d**) with atom numbers. Molecule 2 has atom numbers increased by 10

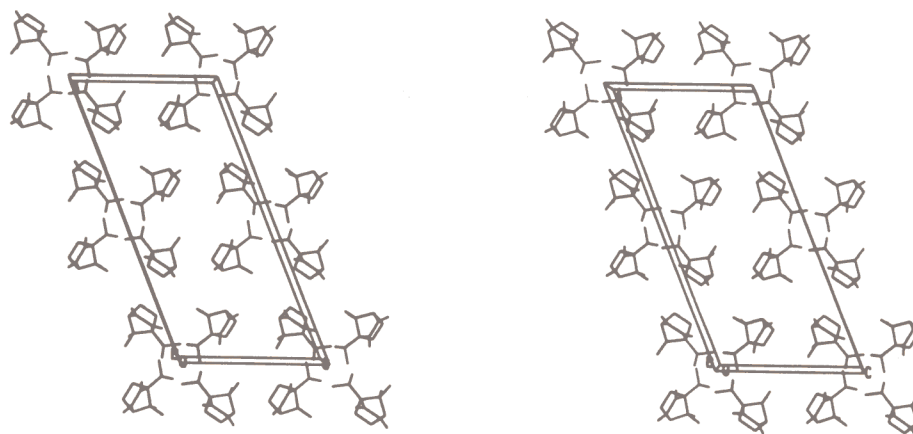


Figure 2. Crystal packing of molecules of compound (**1d**) in the unit cell viewed along the *b*-axis

Table 1. C.d. data of α -diketones

Comp.	Medium ^a	λ/nm^b	$10^{-3}[\theta]/\text{deg cm}^2 \text{ dmol}^{-1}$	λ/nm^b	$10^{-3}[\theta]/\text{deg cm}^2 \text{ dmol}^{-1}$
(1a)	C	484	-1.40	293	0.97
(1d)	D	482.5	-2.28	294	0.33
	K	473	0.70 ^c	310	(+) ^d
(1e)	D	479	-1.67	292	1.12
(1f)	C	509	0.18	292	0.79
		488.5	-1.40		
(1g)	C	487.5	-5.94	280	3.35
(1h)	C	477	-9.32	280	3.87
(1i)	D	472	-3.53	297	0.88
(1j)	CD	476.5	-3.34	268	0.47
(1l)	D	466	-4.04	305.5	5.82
(1m)	D	465	-2.00	288	2.04
(1n)	D	465	-3.78	306	6.34
(1o)	CD	485	-4.53	296	4.45
(1p)	D	462	-2.78	297	2.38
(2) ^e	C	506	-1.61	283	3.36
(3) ^e	C	488	0.80	294	-0.32
(4) ^e	C	491	-1.17	296	-1.62
(5) ^e	C	484	-1.39	293	0.97
(6)	A	501	-1.17	291	3.41
		430	0.06		
	C	508	-1.30	295	2.72
		455	0.30		

^a C, cyclohexane; D, dioxane; CD, cyclohexane-dioxane (4:1); A, acetonitrile; K, KBr disc. ^b The highest-intensity vibronic band. ^c Value determined according to ref. 11. ^d C.d. sign only was determined. ^e Data are not corrected for optical purity.

is very sensitive to substituents. Although earlier works^{3,4,11} suggested that inherent chirality of the skewed diketone group is a source of optical activity in compound (**1a**), in the light of our X-ray results which show that the diketone chromophore is essentially planar, the main source of rotatory strength appears to be a vicinal effect of substituents, and the C.E. magnitude varies along with their polarizabilities.¹³ The largest C.E. exhibited by (**1h**) suggests that bromine atom acts as strong vicinal perturber. Also, absorption spectra furnish evidence against inherent chirality of the dione chromophore in solution. It is well known that the energy of the first $n \rightarrow \pi^*$ transition is determined by CO/CO dihedral angle.^{14,25} In the symmetric compound (**1b**) the chromophore is expected to be planar. The same wavelength of absorption maxima exhibited by diones (**1a**) and (**1b**) [λ_{max} , 483 (ε 39) and 483 nm (40), respectively, in cyclohexane] point to the similar geometry of these compounds. This simple picture is overshadowed by results from solid-state spectra: Lightner *et al.*¹¹ have measured c.d. spectra of compounds (**1a**), (**1c**), and (**1h**) in KBr discs and have established that the C.E. associated with the long-wavelength transition changes sign in the solid state for (**1a**) and (**1c**), i.e. is positive for (**1a**) but remains invariant for (**1h**). However, the C.E. sign for the 300 nm transition is unchanged under varying conditions. As one of possible explanations they proposed a change in helicity of the dione torsion angle from *P* in the solid to *M* in solution for dione (**1a**). They have referred to crystal data for compound (**1a**), which shows that one of the two molecules in the asymmetric unit exhibits small *P* dione chirality¹⁷ as was mentioned in the previous section. However, recent theoretical calculations for skewed α -diketones predict a negative C.E. sign for the lowest-energy transition, in agreement

with experiment.* Also, it is rather improbable that a deuterium atom at C-1 of (1c) would induce dione non-planarity. To clarify this problem we measured the c.d. of compound (1d) in a KBr disc. In contrast to (1a), all molecules of (1d) are essentially planar in the crystal. However, the c.d. spectra of diones (1a) and (1d) in the solid state are very similar, *i.e.* (1d) also changes its C.E. sign at 480 nm in the crystal state. The variation of c.d. sign between solid and solution states is probably connected with the association of molecules in the condensed phase and is characteristic for small C.E.s. A similar effect is frequently observed for aggregated molecules of monoketones in low temperatures.²⁶

The planar α -diketone moiety possesses C_{2v} symmetry and for this type of chromophore Schellman's symmetry rules predict that the quadrant sector rule governs the sign and magnitude of the C.E.²⁷ However, such a rule is only the minimal symmetry requirement and detailed considerations based on dynamic coupling models lead to the octant rule as a proper sector rule.²⁸ Calculations of the rotatory strength for diones (1a) and (1h) based on this model show that the formulae equivalent to the simple octant rule are capable of reproducing both the magnitude and the sign of the C.E.¹³ Since for compounds (2)–(5) the chromophore is expected to be planar, and the methyl substituents have unequivocal locations in space, these compounds were chosen for testing the rule. Indeed, inspection of c.d. spectra of diones (2)–(4) (reproduced in Figure 3) shows convincingly that the octant rule with the signs opposite to those known for monoketones correctly predicts the C.E. sign of planar α -diketones, *i.e.* *exo*-methyl located in back lower right octant is responsible for the negative c.d. near 500 nm of dione (2), but that the *endo*-methyl in the corresponding front octant (close to the nodal surface)[†] contributes the positive sign to the c.d. of compound (3) at the same wavelength. Analogously, the C.E. signs for (1a), (1d–p), and (5) are in agreement with the rule (Figure 4). Although the C-10 methyl group is closer to the chromophore than is the *exo*-methyl, it is also closer to the nodal surface, and therefore acts as a weaker perturber, and so (1a) exhibits a smaller C.E. magnitude than does (2).

The higher-energy c.d. band with distinct fine structure generally shows opposite C.E. sign to that of the lowest energy as a result of opposite symmetry of the molecular orbitals involved in two $n \rightarrow \pi^*$ transitions. One of the rare exceptions is dione (4), which shows positive C.E. signs in both 300 and 500 nm regions. Compound (4) presents also an example of non-additive contributions from the substituents; its c.d. spectrum is not the simple sum of the c.d. spectra of compounds (2) and (3) that one could expect.

The complex picture presents dione (6) showing bisignate C.E. within the region of $n_+ \rightarrow \pi_-^*$ transition (Figure 5). The solvent dependence may suggest conformational equilibrium; this is, however, rather improbable for such a rigid and closely structurally related compound to (1a). A comparison of the absorption spectra of compounds (1a) and (6) reveals different vibronic structure of the long-wavelength bands. Probably, in the case of compound (6), at least two vibronic modes contribute to the lowest-energy electronic transition, hence the possible explanation of the bisignate C.E. is the vibronic coupling effect.²⁹ The long-wavelength part of the C.E.

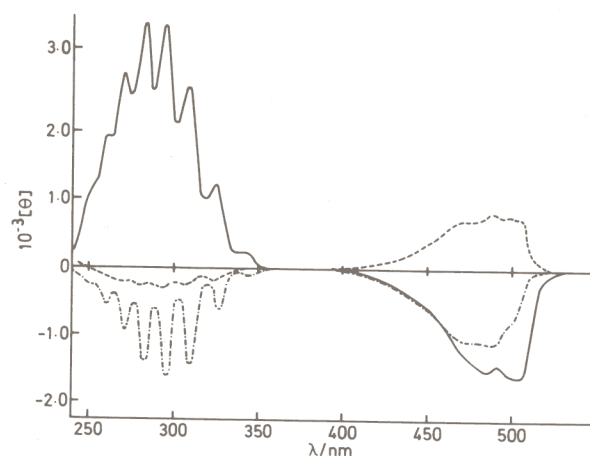


Figure 3. C.d. spectra of α -diketones (2) (—), (3) (---), and (4) (— · —) in cyclohexane ($[\theta]$ in $\text{deg cm}^2 \text{dmol}^{-1}$)

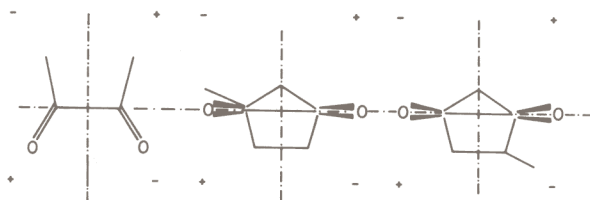


Figure 4. The octant projections of molecules (1a) and (2)

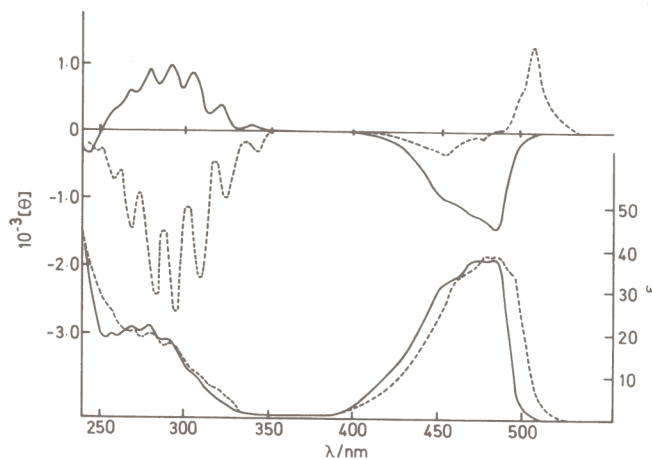


Figure 5. C.d. (upper curves) and u.v. spectra of compounds (1a) (—) and (6) (---) ($[\theta]$ in $\text{deg cm}^2 \text{dmol}^{-1}$)

corresponds to an 'allowed' c.d. and agrees with the octant rule. The similar bisignate and solvent-sensitive c.d. curves are common features of rigid monoketones with isofenchone and *epi*-isofenchone skeletons.³⁰

In conclusion it is stressed that the c.d. spectra of bicyclo[2.2.1]heptane-2,3-diones can be explained assuming that the chromophore is planar in solution. The C.E. sign is governed by vicinal effect of substituents and can be predicted according to the simple octant rule.

Experimental

C.d. spectra were recorded on a Jasco J-20 spectropolarimeter. U.v. measurements were performed on a Beckman 3600

* (—)-Carbocamphenilone, with dione torsion angle of 33.9° (*P*-chirality from *X*-ray), shows a negative c.d. band at 393 ($\Delta\epsilon -1.59$) and a positive one at 287 nm ($\Delta\epsilon +1.25$).⁷

† Lightner *et al.* explained the c.d. of *exo*-2-methylbicyclo[2.2.1]heptan-7-one by assuming a similar location of the methyl group in space to that of compound (3) (D. A. Lightner and D. E. Jackman, *J. Am. Chem. Soc.*, 1974, **96**, 1938; D. A. Lightner, J. K. Gawroński, and T. D. Bouman, *ibid.*, 1980, **102**, 1983).

spectrophotometer. N.m.r. spectra were taken with a Varian EM-360A (60 MHz) spectrometer with tetramethylsilane as internal standard. I.r. absorptions were obtained with a Zeiss IR-10 spectrophotometer and mass spectra (field desorption) were taken on a Varian MAT-711 mass spectrometer. M.p.s were measured on a Melt-Temp capillary apparatus and are uncorrected.

The syntheses of compounds (1b) and (1i) have been published elsewhere.²³ α -Diketones (2)–(5) are very sensitive to moisture and their spectra were measured on freshly prepared samples.

(1R)-1-Acetoxyethyl-7,7-dimethylbicyclo[2.2.1]heptane-2,3-dione (1e).—10-Acetoxyamphor (19)²¹ (10.5 g, 50 mmol) and selenium dioxide (5.55 g, 50 mmol) were refluxed in acetic acid (50 ml) for 10 h. The reaction mixture was filtered and the filtrate was evaporated to dryness. The residue was dissolved in diethyl ether, washed with aqueous NaHCO₃, dried (MgSO₄), and evaporated. Crystallization of the residue from toluene–hexane gave the *title compound* 8.8 g, 81%, m.p. 88 °C; $[\alpha]_D^{20}$ –105.0° (c 2 in CHCl₃); λ_{\max} (cyclohexane) 480 (ε 35) and 280 nm (22); δ_H (CCl₄) 4.28 (2 H, s, CH₂O), 2.52 (1 H, m, CHCO), 2.3–1.4 (4 H, complex m), 2.02 (3 H, s, MeCO), 1.15 (3 H, s, Me), and 1.06 (3 H, s, Me) (Found: C, 64.4; H, 7.3. C₁₂H₁₆O₄ requires C, 64.3; H, 7.2%).

(1R)-1-Hydroxymethyl-7,7-dimethylbicyclo[2.2.1]heptane-2,3-dione (1d).—This *hydroxy dione* was prepared by hydrolysis of acetate (1e) with boiling 20% hydrochloric acid for 2 h; m.p. 205 °C (from ethyl acetate–hexane); $[\alpha]_D^{20}$ –173° (c 2 in CHCl₃); λ_{\max} (cyclohexane–dioxane 4:1) 474 (ε 41) and 280 nm (36); ν_{\max} (CHCl₃) 3 610 br (OH), 1 775 (CO), and 1 762 cm^{–1} (CO); δ_H (CDCl₃) 3.95 (2 H, AB system, *J* 12 Hz, CH₂O), 2.55 (1 H, m, CHCO), 2.40 (1 H, s, OH), 2.2–1.5 (4 H, complex m), 1.10 (3 H, s, Me), and 1.02 (3 H, s, Me) (Found: C, 66.0; H, 7.6. C₁₀H₁₄O₃ requires C, 65.9; H, 7.7%).

(1S)-1-Fluoro-7,7-dimethylbicyclo[2.2.1]heptane-2,3-dione (1f).—1-Aminoapocamphor hydrochloride (21)²⁴ (3.06 g, 20 mmol) was dissolved in hydrogen fluoride–pyridine complex (20 ml) and sodium nitrite (2 g) was added during 0.5 h to the stirred, cooled mixture. After being stirred for an additional 1 h, the reaction mixture was poured into water and extracted with benzene. The extract was dried (Na₂SO₄), decolorized with silica gel, and evaporated. The residue (1.7 g) was dissolved in acetic acid (10 ml), selenium dioxide (2.0 g) was added, and the mixture was refluxed for 12 h, then evaporated; the residue was dissolved in diethyl ether, and the solution was filtered, washed with aqueous NaHCO₃, and dried (Na₂SO₄). After evaporation of ether, the residue was chromatographed on silica gel with elution of the product with hexane–chloroform (1:1). The *title product* (0.87 g) was crystallized from hexane, m.p. 166 °C; $[\alpha]_D^{20}$ –125° (c 1 in CHCl₃); λ_{\max} (cyclohexane) 486 (ε 38) and 281 nm (25); δ_H (CDCl₃) 2.6 (1 H, m, CHCO), 2.3–1.3 (4 H, complex m), 1.19 (3 H, s, Me), and 1.03 (3 H, s, Me) (Found: C, 63.2; H, 6.1%; M⁺, 170. C₉H₁₁FO₂ requires C, 63.5; H, 6.05%; M, 170).

(1S)-1-Chloro-7,7-dimethylbicyclo[2.2.1]heptane-2,3-dione (1g).—To a cooled, stirred solution of the salt (21) (3.8 g, 20 mmol) in conc. hydrochloric acid (20 ml) was added sodium nitrite (2 g) during 0.5 h. After being stirred for an additional 1 h, the mixture was worked up in an analogous manner to (1f). The *title product* (0.34 g) was crystallized from heptane, m.p. 206 °C; $[\alpha]_D^{20}$ –309° (c 2 in CHCl₃); δ_H (CDCl₃) 2.73 (1 H, m, CHCO), 2.4–1.4 (4 H, complex m), 1.13 (3 H, s, Me), and 0.97 (3 H, s, Me) (Found: C, 57.9; H, 6.0%; M⁺, 186 and 188. C₉H₁₁ClO₂ requires C, 57.9; H, 5.9%; M, 186 and 188).

(1S)-1-Bromo-7,7-dimethylbicyclo[2.2.1]heptane-2,3-dione (1h).—Diketone (1h) was obtained by oxidation of bromo ketone (24)³¹ with selenium dioxide in acetic acid (18 h), m.p. 204 °C (from heptane); $[\alpha]_D^{20}$ –368° (c 1 in CHCl₃) {lit.,⁹ m.p. 201.5–202 °C; $[\alpha]_D^{20}$ –366° (c 0.38 in CHCl₃)}; λ_{\max} (cyclohexane) 475 (ε 50) and 310 nm (26).

Methyl (1S)-7,7-Dimethyl-2,3-dioxobicyclo[2.2.1]heptane-1-carboxylate (1j).—The ester (1j) was obtained by esterification of acid (1i)²³ with diazomethane, m.p. 94–95 °C (from toluene–hexane); $[\alpha]_D^{20}$ –183° (c 2 in CHCl₃); δ_H (CCl₄) 3.78 (3 H, s, CO₂Me), 2.50 (1 H, m, CHCO), 2.4–1.4 (4 H, complex m), 1.16 (3 H, s, Me), and 1.12 (3 H, s, Me) (Found: C, 63.1; H, 7.0. C₁₁H₁₄O₄ requires C, 62.9; H, 6.7%).

t-Butyl (1S)-7,7-Dimethyl-2,3-dioxobicyclo[2.2.1]heptan-1-ylcarbamate (1l).—Acid (1i)²³ (5.9 g, 30 mmol) was refluxed in thionyl chloride (20 ml) for 1 h; the mixture was evaporated, the residue was dissolved in CCl₄, and the solvent was evaporated off. The resulting acid chloride was dissolved in acetone (20 ml), the solution was cooled to 0 °C, a solution of sodium azide (2.6 g, 40 mmol) in water (10 ml) was added, and the mixture was stirred and cooled for 1.5 h. Acetone was evaporated off and the remanent acid azide was extracted with toluene (30 ml). The organic layer was dried and then heated to begin the reaction. After the evolution of CO₂ ceased, the mixture was refluxed for 15 min and evaporated to dryness. The resulting isocyanate (1k) was dissolved in dry t-butyl alcohol (60 ml) and the solution was refluxed for 12 h. The solvent was evaporated off and the *title product* was crystallized from ethyl acetate–hexane (yield (4.7 g, 50% overall), m.p. 158 °C; $[\alpha]_D^{20}$ –185° (c in CHCl₃); ν_{\max} (CCl₄) 3 420 (NH), 1 780 (CO), 1 765 (CO), and 1 725 cm^{–1} (CONH); δ_H (CDCl₃) 5.43 (1 H, br, CONH), 2.67 (1 H, m, CHCO), 2.5–1.6 (4 H, complex m), 1.22 (3 H, s, Me), 1.13 (9 H, s, OCM₃), and 0.96 (3 H, s, Me) (Found: C, 62.9; H, 7.7; N, 5.5. C₁₄H₂₁NO₄ requires C, 62.9; H, 7.9; N, 5.2%).

(1S)-1-Amino-7,7-dimethylbicyclo[2.2.1]heptane-2,3-dione Trifluoroacetate (1m).—Compound (1l) (1.34 g, 5 mmol) was dissolved in TFA (5 ml) and after 15 min the solution was evaporated to dryness. The residue was crystallized after addition of chloroform (yield 1.4 g, 99%), m.p. 144 °C (with decomp.) (Found: C, 47.2; H, 5.05; N, 5.0. C₁₁H₁₄F₃NO₄ requires C, 47.0; H, 5.0; N, 5.0%).

(1S)-1-Acetamido-7,7-dimethylbicyclo[2.2.1]heptane-2,3-dione (1n).—1-Acetamidoapocamphor (25), obtained by action of acetyl chloride on the amine (21),²⁴ was oxidized with selenium dioxide in acetic acid in analogous manner to the preparation of acetate (1e), to give the *title product* m.p. 125 °C (from toluene); $[\alpha]_D^{20}$ –183° (c 2 in CHCl₃); ν_{\max} (CCl₄) 3 410 (NH), 1 785 (CO), 1 768 (CO), and 1 700 cm^{–1} (CONH); δ (CDCl₃) 6.37 (1 H, s, CONH), 2.51 (1 H, m, CHCO), 2.3–1.4 (4 H, m), 1.98 (3 H, s, MeCO), 1.12 (3 H, s, Me), and 0.88 (3 H, s, Me) (Found: C, 62.9; H, 7.3; N, 6.75. C₁₁H₁₅NO₃ requires C, 63.1; H, 7.2; N, 6.7%).

(1R)-7,7-Dimethyl-1-phenylbicyclo[2.2.1]heptan-2-one (26).—Ketopinic acid (20)²² (5.46 g, 30 mmol) and lead tetra-acetate (5 g) were refluxed in benzene (800 ml) for 3 h under argon. The reaction mixture was concentrated to ca. 100 ml, filtered, and the filtrate was washed with aqueous NaHCO₃, dried (MgSO₄), and evaporated to dryness. Crystallization from methanol gave the *title product* (0.67 g, 30%), m.p. 86–87 °C; $[\alpha]_D^{20}$ +121° (c 3 in EtOH); δ_H (CDCl₃) 7.18 (5 H, s, Ph), 2.7–2.3 (2 H, m, CH₂CO), 2.2–1.2 (5 H, m), 0.83 (3 H, s, Me), and 0.78 (3 H, s, Me) (Found: C, 83.8; H, 8.4. C₁₅H₁₈O requires C, 84.1; H, 8.5%).

(1R)-7,7-Dimethyl-1-phenylbicyclo[2.2.1]heptane-2,3-dione (10).—Ketone (26) was oxidized with selenium dioxide in acetic acid analogously to the preparation of acetate (1e); the *title product* had m.p. 193 °C (from chloroform–hexane); $[\alpha]_D^{20}$ –167° (c 0.5 in CHCl₃); δ_H (CDCl₃) 7.16 (5 H, m, Ph), 2.65 (1 H, m, CHCO), 2.5–1.3 (4 H, m), 0.86 (3 H, s, Me), and 0.84 (3 H, s, Me) (Found: C, 78.8; H, 7.1. C₁₅H₁₆O₂ requires C, 78.9; H, 7.1%).

(1S)-7,7-Dimethyl-2,3-dioxobicyclo[2.2.1]heptane-1-carboxamide (1p).—Acid (1i)²³ (1.96 g, 10 mmol) was refluxed in thionyl chloride (10 ml) for 1 h, then the mixture was evaporated to dryness, the residue was dissolved in chloroform, and the solution treated with gaseous ammonia. The reaction mixture was washed with water, dried (MgSO₄), and evaporated, and the residue was crystallized from toluene to obtain the *title product* (1.30 g, 67%), m.p. 188 °C; $[\alpha]_D^{20}$ 235° (c 1 in CHCl₃); ν_{\max} (CHCl₃) 3 510 (NH), 3 490br (NH), 1 780 (CO), 1 765 (CO), 1 700, 1 685, and 1 598 cm⁻¹ (CONH₂) (Found: C, 61.3; H, 6.8; N, 7.0. C₁₀H₁₃NO₃ requires C, 61.5; H, 6.7; N, 7.2%).

(1S)-exo-Bicyclo[2.2.1]hept-5-ene-2-carboxylic Acid (7a).—The resolution of racemic (7a) with (–)-1-phenylethylamine (five crystallizations of the salt from ethanol) gave leavorotatory acid (7a), m.p. 36–38 °C; $[\alpha]_D^{20}$ –12.1° (c 5 in EtOH) (71% optical purity) {lit.,¹⁸ m.p. 37–39 °C; $[\alpha]_D$ –12.4° (in EtOH)}.

(1S)-exo-5-Hydroxymethylbicyclo[2.2.1]hept-2-ene (7b).—Reduction of *exo*-acid (7a) with lithium aluminium hydride in diethyl ether gave *exo*-alcohol (7b), b.p. 99–101 °C at 14 mmHg; $[\alpha]_D^{20}$ –11.2° (neat) {lit.,¹⁸ b.p. 101–101.5 °C at 22 mmHg; $[\alpha]_D$ –12.4° (c 5.59 in EtOH)}.

(1R)-exo-5-Methylbicyclo[2.2.1]hept-2-ene (7d).—Alcohol (7b) was treated with toluene-*p*-sulphonyl chloride in pyridine to give the toluene-*p*-sulphonate (7c), m.p. 54–57 °C (from hexane); $[\alpha]_D^{20}$ –13.2° (c 4 in C₆H₆); δ_H (CDCl₃) 8.10 and 7.80 (4 H, m, C₆H₄), 6.25 (2 H, m, CH=CH), 4.04 (2 H, dd, CH₂O), 2.90 (2 H, m, 2 × CHCH=), 2.39 (3 H, s, Me), and 1.9–1.0 (5 H, complex m). Reduction of tosylate (7c) with lithium aluminium hydride in diglyme–diethyl ether mixture* for 4 h gave hydrocarbon (7d), b.p. 116 °C {lit.,³² (racemate) 116–116.7 °C}; $[\alpha]_D^{20}$ –15.1° (neat) {lit.,³³ $[\alpha]_D^{25}$ 17.8° (c 6.15 in EtOH)}; δ_H (CCl₄) 6.23 (2 H, m, CH=CH), 2.91 (1 H, m, CHCH=), 2.48 (1 H, m, CHCH=), 1.6–1.0 (5 H, complex m), and 1.06 (3 H, d, Me).

(1R)-exo-5-Methylbicyclo[2.2.1]heptane-2,3-dione (2).—Hydrocarbon (7d) (2.7 g, 25 mmol) was converted into a mixture of ketones (10) according to the procedure of Brown *et al.*²⁰ The crude alcohols (10) were oxidized with Jones' reagent; after evaporation of acetone, water was added and the product was extracted with pentane. The extract was washed with water, dried (MgSO₄), and evaporated, and the resulting mixture was distilled to obtain ketones (14) (2.5 g), b.p. 90–95 °C at 45 mmHg. Oxidation of ketones (14) with selenium dioxide in boiling acetic acid for 1 h, and subsequent work-up of the reaction mixture analogously to the preparation of acetate (1e), afforded crude dione (2). Distillation (b.p. 115 °C at 14 mmHg), and crystallization from hexane, gave dione (2) (0.8 g), m.p. 65–68 °C; $[\alpha]_D^{20}$ –118° (c 3 in C₆H₆); δ_H (CDCl₃) 2.98 (1 H, d, CHCO), 2.62 (1 H, s, CHCO), 2.3–1.2 (5 H, complex m), and 1.13 (3 H, d, Me) (Found: C, 69.3; H, 7.55%; *M*⁺, 138. C₈H₁₀O₂ requires C, 69.55; H, 7.3%; *M*, 138).

(1S)-endo-Bicyclo[2.2.1]hept-5-ene-2-carboxylic Acid (8a).—The resolution of racemic acid (8a) as described for the isomer (7a) gave leavorotatory acid (8a), b.p. 129–132 °C at 12 mmHg; $[\alpha]_D^{20}$ –116° (c 0.5 in EtOH) (81% optical purity) {lit.,¹⁹ b.p. 139–140 °C at 20 mmHg; $[\alpha]_D$ –119° (c 1.4 in 95% EtOH)}.

(1S)-endo-5-Hydroxymethylbicyclo[2.2.1]hept-2-ene (8b).—Alcohol (8b) was obtained analogously to its isomer (7b), and had b.p. 90–92 °C at 12 mmHg; $[\alpha]_D^{20}$ –68° (c 1 in EtOH) {lit.,¹⁹ b.p. 92–96 °C at 14 mmHg; $[\alpha]_D^{20}$ –70.0° (c 1 in 99% EtOH)}.

(1R)-endo-5-Methylbicyclo[2.2.1]hept-2-ene (8d).—Alcohol (8b) was acylated similarly to its isomer (7b) to give toluene-*p*-sulphonate (8c), m.p. 42–43 °C (from hexane); δ_H (CCl₄) 7.78 and 7.30 (4 H, m, C₆H₄), 6.09 and 5.76 (2 H, m, CH=CH), 3.56 (2 H, m, CH₂O), 2.84 (2 H, m, 2 × CHCH=), 2.44 (3 H, s, Me), and 2.3–1.1 (5 H, complex m). Compound (8c) was reduced similarly to its isomer (7c) to afford hydrocarbon (8d), b.p. 112–115 °C; $[\alpha]_D^{20}$ –46° (c 5 in CHCl₃) {lit.,¹⁸ b.p. 114–115.5 °C; $[\alpha]_D^{20}$ –47.8° (c 8.95 in CHCl₃)}.

(1R)-endo-5-Methylbicyclo[2.2.1]heptane-2,3-dione (3).—Hydrocarbon (8d) was converted into a mixture of ketones (15) as described for the preparation of their isomers (14); the mixture (15) had b.p. 85–90 °C at 35 mmHg. Oxidation of ketones (15) with selenium dioxide as described for compound (2) provided dione (3), m.p. 38–40 °C (from hexane); $[\alpha]_D^{20}$ +110° (c 1 in C₆H₆); δ_H (CCl₄) 2.87 (2 H, m, 2 × CHCO), 2.4–0.9 (5 H, complex m), and 0.93 (3 H, d, Me) (Found: C, 69.35; H, 7.4%; *M*⁺, 138. C₈H₁₀O₂ requires C, 69.55; H, 7.3%; *M*, 138).

(1S)-endo-2-Methylbicyclo[2.2.1]hept-5-ene-2-carboxylic Acid (9a).—The resolution of racemic acid (9a) with (–)-1-phenylethylamine (two crystallizations of the salt from ethanol) gave dextrorotatory acid (9a), m.p. 45–47 °C; $[\alpha]_D^{20}$ +58.5° (c 5 in EtOH) (87% optical purity) {lit.,¹⁸ m.p. 47–48 °C; $[\alpha]_D$ +67.3° (in EtOH)}.

(1S)-5,5-Dimethylbicyclo[2.2.1]hept-2-ene (9d).—Acid (9a) was converted into hydrocarbon (9d) following the procedure of Berson *et al.*,¹⁸ the product had b.p. 128–132 °C; $[\alpha]_D^{20}$ +35.5° (c 3 in C₆H₆) {lit.,¹⁸ b.p. 128–131 °C; $[\alpha]_D$ +27° (in C₆H₆)}.

(1S)-5,5-Dimethylbicyclo[2.2.1]heptane-2,3-dione (4).—Hydrocarbon (9d) (7.1 g, 50 mmol) was converted into a mixture of ketones (16) (5.1 g), b.p. 96–98 °C at 40 mmHg. Oxidation of ketones (16) with selenium dioxide as described for the preparation of dione (2) afforded dione (4) (2.1 g), m.p. 107 °C (from hexane); $[\alpha]_D^{20}$ –147° (c 1 in C₆H₆); δ_H (CCl₄) 2.87 (1 H, d, CHCO), 2.50 (1 H, s, CHCO), 2.5–1.1 (4 H, complex m), 1.19 (3 H, s, Me), and 0.98 (3 H, s, Me) (Found: C, 69.9; H, 8.15%; *M*⁺, 152. C₉H₁₂O₂ requires C, 71.0; H, 7.95%; *M*, 152).

Methyl (1R)-exo-5,6-Dioxobicyclo[2.2.1]heptane-2-carboxylate (5).—Acid (7a) was converted into mixture of keto acids (17) following the procedure of Beckmann *et al.*³⁴ for the racemic compound. Acid (17) was esterified with ethereal diazomethane to afford ester (18), which was then oxidized with selenium dioxide, as described for the preparation of compound (2), to obtain ester (5), which was sublimed at 12 mmHg, m.p. 115–117 °C; $[\alpha]_D^{20}$ –231° (c 0.65 in C₆H₆); δ_H 3.83 (3 H, s, CO₂Me), 3.35 (1 H, s), 3.17 (1 H, m), and 3.0–1.8 (5 H, complex m) (Found: C, 59.1; H, 5.7. C₉H₁₀O₄ requires C, 59.3; H, 5.5%).

* Diglyme is MeO(CH₂CH₂O)₂Me.

Table 2. Atomic co-ordinates ($\times 10^4$) for compounds (**1d**) and (**1h**)

	x	y	z
Compound (1d), Molecule 1			
C(1)	5 966(2)	2 370(0)	2 913(5)
C(2)	6 008(3)	4 393(12)	3 449(6)
O(2)	5 669(2)	5 760(9)	3 112(6)
C(3)	6 563(3)	4 425(11)	4 487(6)
O(3)	6 748(2)	5 849(9)	5 149(5)
C(4)	6 813(3)	2 427(12)	4 531(6)
C(5)	6 418(4)	1 099(13)	4 915(7)
C(6)	5 852(3)	990(13)	3 828(7)
C(7)	6 623(3)	1 997(10)	3 189(5)
C(8)	6 882(3)	3 478(13)	2 559(7)
C(9)	6 748(3)	-117(12)	2 897(8)
C(10)	5 557(3)	2 075(16)	1 629(7)
O(10A)	4 975(3)	2 214(15)	1 386(8)
O(10B)	5 613(4)	3 332(17)	928(8)
Molecule 2			
C(11)	3 875(3)	7 377(11)	1 069(5)
C(12)	3 648(3)	9 476(11)	947(5)
O(12)	3 704(3)	10 844(10)	359(5)
C(13)	3 283(3)	9 548(11)	1 729(6)
O(13)	3 022(2)	10 967(9)	1 848(4)
C(14)	3 337(3)	7 500(11)	2 248(6)
C(15)	2 978(3)	6 209(11)	1 181(6)
C(16)	3 345(3)	6 109(13)	379(6)
C(17)	3 968(3)	6 997(11)	2 404(6)
C(18)	4 402(3)	8 392(13)	3 293(6)
C(19)	4 132(3)	4 860(12)	2 810(7)
C(20)	4 385(3)	7 052(14)	681(6)
O(20A)	4 301(4)	7 239(15)	-495(8)
O(20B)	4 768(4)	8 257(15)	1 105(9)
Compound (1h)			
C(1)	2 292(9)	2 192(9)	2 562(15)
C(2)	1 939(9)	3 533(11)	2 175(22)
O(2)	1 013(7)	3 962(8)	2 070(20)
C(3)	3 081(11)	4 190(12)	2 000(23)
O(3)	3 233(11)	5 272(7)	1 715(20)
C(4)	3 968(10)	3 176(11)	2 373(23)
C(5)	3 853(13)	2 902(14)	4 441(20)
C(6)	2 720(11)	2 195(12)	4 556(18)
C(7)	3 384(9)	2 043(11)	1 422(16)
C(8)	4 049(12)	853(12)	1 709(22)
C(9)	3 204(14)	2 276(15)	-631(18)
Br	1 094(1)	1 030(1)	2 092(2)

Table 3. Bond lengths (Å) and angles ($^\circ$) for compounds (**1d**) and (**1h**), with e.s.d.s in parentheses

	(1d), mol. 1	(1d), mol. 2	(1h)
C(1)–C(2)	1.499(8)	1.516(10)	1.545(16)
C(1)–C(6)	1.549(11)	1.542(9)	1.543(16)
C(1)–C(7)	1.580(9)	1.556(10)	1.538(15)
C(1)–X(10) ^a	1.519(9)	1.533(12)	1.924(10)
C(2)–C(3)	1.490(8)	1.538(11)	1.526(18)
C(2)–O(2)	1.220(9)	1.204(10)	1.186(13)
C(3)–C(4)	1.482(11)	1.504(10)	1.544(18)
C(3)–O(3)	1.226(9)	1.200(10)	1.211(16)
C(4)–C(5)	1.531(12)	1.539(9)	1.546(22)
C(4)–C(7)	1.533(9)	1.561(9)	1.575(16)
C(5)–C(6)	1.538(9)	1.564(13)	1.540(18)
C(7)–C(8)	1.537(12)	1.537(9)	1.528(16)
C(7)–C(9)	1.532(11)	1.532(11)	1.537(19)
C(10)–O(10A)	1.383(11)	1.357(13)	
C(10)–O(10B)	1.242(15)	1.218(13)	
C(2)–C(1)–C(6)	104.2(6)	104.4(5)	105.0(10)
C(2)–C(1)–C(7)	98.9(4)	99.3(6)	103.0(9)
C(2)–C(1)–X(10)	118.1(5)	115.5(7)	113.2(7)
C(6)–C(1)–C(7)	102.0(4)	103.5(6)	103.9(9)
C(6)–C(1)–X(10)	114.2(5)	114.1(6)	114.1(8)
C(7)–C(1)–X(10)	117.0(6)	117.9(5)	116.3(8)
C(1)–C(2)–C(3)	105.6(6)	105.0(6)	102.9(9)
C(1)–C(2)–O(2)	128.2(6)	130.9(8)	129.1(11)
O(3)–C(2)–O(2)	126.2(7)	124.1(7)	128.0(11)
C(2)–C(3)–C(4)	105.7(6)	104.0(6)	104.0(9)
C(2)–C(3)–O(3)	124.6(7)	125.1(7)	126.9(13)
C(4)–C(3)–O(3)	129.8(6)	130.9(7)	129.0(14)
C(3)–C(4)–C(5)	103.4(7)	103.9(5)	104.6(13)
C(3)–C(4)–C(7)	100.0(5)	100.5(6)	100.9(9)
C(5)–C(4)–C(7)	102.9(5)	103.5(6)	104.0(10)
C(4)–C(5)–C(6)	105.7(6)	103.9(6)	103.0(10)
C(1)–C(6)–C(5)	102.7(6)	103.5(6)	103.3(10)
C(1)–C(7)–C(4)	94.9(5)	94.7(5)	92.3(9)
C(1)–C(7)–C(8)	113.1(5)	114.5(6)	116.2(10)
C(1)–C(7)–C(9)	112.8(5)	113.9(6)	113.4(10)
C(4)–C(7)–C(8)	111.8(6)	112.1(6)	112.5(9)
C(4)–C(7)–C(9)	114.1(6)	112.7(6)	111.2(12)
C(8)–C(7)–C(9)	109.6(7)	108.5(5)	110.1(11)
C(1)–C(10)–O(10A)	118.1(8)	118.6(7)	
C(1)–C(10)–O(10B)	113.3(8)	113.3(9)	

^a X(10) denotes C(10) [or C(20)] in (**1d**) or Br in (**1h**).

(1R)-1,5,5-Trimethylbicyclo[2.2.1]heptane-2,3-dione (**6**).—Compound (**6**) was obtained by selenium dioxide oxidation of isofenchone according to the procedure of Gervais and Rassat,³⁵ and had m.p. 69.5–70 °C (from hexane) (lit.,³⁶ 69–70 °C); λ_{max} (cyclohexane) 484 (ε 38) and 280 nm (19); δ_{H} (CCl₄) 2.47 (1 H, s, CHCO), 2.3–1.4 (4 H, complex m), 1.23 (3 H, s, Me), 1.17 (3 H, s, Me), and 0.96 (3 H, s, Me).

X-Ray Structure Analysis.—Crystal data for hydroxy dione (**1d**). C₁₀H₁₄O₃, $M = 182.22$, monoclinic, space group C2, $a = 25.12(2)$, $b = 6.76(1)$, $c = 12.03(1)$ Å, $\beta = 111.7^\circ$, $V = 1 898$ Å³, $Z = 8$ (two molecules per asymmetric unit), $D = 1.275$ g cm⁻³, $\lambda(\text{Cu-K}\alpha) = 1.5418$ Å, $\mu = 0.68$ cm⁻¹.

Crystal data for bromo dione (**1h**). C₉H₁₁BrO₂, $M = 231.09$, orthorhombic, space group $P2_12_12_1$, $a = 11.742(4)$, $b = 10.900(3)$, $c = 7.310(3)$ Å, $V = 936$ Å³, $Z = 4$, $D_c = 1.640$ g cm⁻³, $\lambda(\text{Cu-K}\alpha) = 1.5418$ Å, $\mu = 5.30$ cm⁻¹.

The data-collection procedure was the same for both compounds. Preliminary cell dimensions and symmetry were determined from Weissenberg photographs. Intensity data were

collected on a Hilger and Watts four-circle diffractometer up to $\theta = 51^\circ$ using the ω -2 θ scan technique. 1 230 Unique reflections [129 unobserved with $I < 2\sigma(I)$] were measured for compound (**1d**) and 803 unique reflections [65 unobserved with $I < 2.5\sigma(I)$] were collected for compound (**1h**). Corrections were applied for Lorentz and polarization effects, but not for absorption.

Both structures were solved by the MULTAN-80 program³⁷ and refined by full-matrix least-squares procedure, initially with isotropic, and then with anisotropic, thermal parameters for non-hydrogen atoms, using the SHELX-76 program.³⁸ Hydrogen-atom positions were calculated and kept constrained during refinement at a constant distance of 1.08 Å from their parent carbon atoms. Methyl substituents were treated as rigid groups. Only one common isotropic temperature factor was used for all hydrogen atoms. The refinement converged to R 0.072 for (**1d**) and R 0.079 for (**1h**) [$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$]. Maximum height in the final difference Fourier map was 0.27 e Å⁻³ for (**1d**) and 0.60 e Å⁻³ for (**1h**). The hydroxy oxygen atom in compound (**1d**) appeared to be disordered in both symmetrically independent molecules and was refined in two alternative positions with site occupancy factor 0.5.

Table 4. Hydrogen bonds in structure (1d)

	$d(\text{O} \cdots \text{O})$ (Å)
$\text{O}(10\text{A}) \cdots \text{O}(20\text{B})^{\text{i}}$	2.732
$\text{O}(10\text{A}) \cdots \text{O}(20\text{B})^{\text{ii}}$	2.722
$\text{O}(10\text{B}) \cdots \text{O}(20\text{A})^{\text{i}}$	2.716
$\text{O}(20\text{A}) \cdots \text{O}(20\text{B})^{\text{i}}$	2.785

Code for symmetry-related atoms: i, $1 - x, y, -z$; ii, $x, -1 + y, z$.

The final atomic co-ordinates for compounds (1d) and (1h) are listed in Table 2. Bond lengths and angles are given in Table 3. Possible intermolecular hydrogen bonds formed by disordered hydroxy groups in the crystal structure of compound (1d) are listed in Table 4. Tables of isotropic and anisotropic temperature factors are given in supplementary Publication No. 56609 (4 pp.).*

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* For details of the Supplementary Publications Scheme, see Instructions for Authors (1986), in *J. Chem. Soc., Perkin Trans. I*, 1986, issue 1.

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